ELECTROPLATING SOLUTION CONTAINING ORGANIC ACID COMPLEXING AGENT

Cross-Reference to Related Applications

This application is a continuation-in-part of International application PCT/US03/03688 Filed February 7, 2003, a continuation-in-part of U.S. non-provisional application no. 10/277,234 filed October 22, 2002 and claims the benefit of U.S. provisional application no. 60/357,330 filed February 15, 2002.

Background of the Invention

The present invention relates to the deposition of metals and more specifically to the deposition of tin or tin-lead alloys on objects or articles composed of an electroplatable substrate, such as metal, or a composite article having electroplatable and non-electroplatable portions. The present invention also describes a method for inhibiting the fusing of a plurality of such composite articles during electrodeposition. This is relevant to the electroplating of small electrical components that have large surface areas per unit mass and are susceptible to fusing. Of particular interest herein are electrical components such as surface mounted capacitors and resistors that have metal portions as well as ceramic, glass, or plastic portions.

The size of electronic components has been dramatically reduced in recent years. This reduction in size has made these components significantly more difficult to electroplate. Additionally, many surface mount technology (SMT) components have sensitive ceramic portions which can be damaged by highly acidic or highly alkaline solutions. To avoid this problem, neutral or near neutral pH electroplating solutions are desirable.

Neutral or near neutral pH tin and tin/lead alloy electrolytes that are specifically formulated to be compatible with sensitive ceramic SMTs are described in US patents 4,163,700, 4,329,207, 4,640,746, 4,673,470, 4,681,670 and Japanese patent application H02-301588. The formulations described in

these patents include complexing agents of components such as citrates, gluconates, ascorbates or pyrophosphates to complex the tin and/or lead and render them soluble in the solutions at the elevated pHs required.

While Japanese patent application H02-301588 discloses that the baths should be operable over a wide pH range of 2 to 9, the examples illustrate near neutral baths (i.e., a pH of 6 to 7.5). The baths of these examples were found to not be stable at pHs below 6. Thus, an improvement in the stability of these baths is desired and necessary.

The prior art solutions mentioned above have a persistent problem of component coupling or agglomeration during electrodeposition. It is quite common when tin or tin alloy plating small components with flat surfaces that the components tend to cluster together during plating. It is not uncommon when barrel plating SMT components that up to 10% of the load may be coupled (i.e., stuck together). Under some conditions, the entire load fuses together in large lumps. The extent of this problem depends on the plating solution composition as well as plating method and geometry of the components. This problem is particularly pronounced in tin-lead alloy electroplating

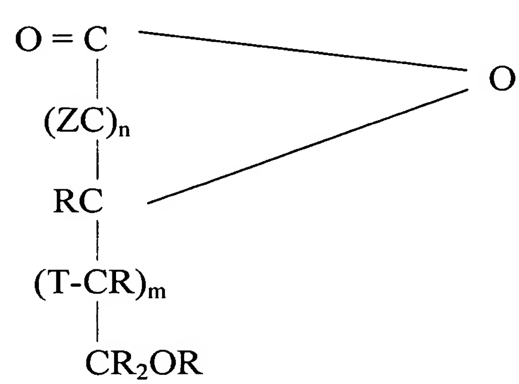
The neutral or near neutral pH tin and tin/lead alloy electrolytes that are specifically formulated to be compatible with sensitive ceramic SMTs have some utility, but they do not address the issue of part agglomeration or fusing. This is a particularly significant problem when the parts are of relatively small size. The present invention now provides a solution and process that overcomes this problem.

Summary of the Invention

The present invention relates to a solution for use in connection with the deposition of one or more metals on electroplatable substrates. This solution comprises water; a metal ion in an amount sufficient to provide a metal deposit

on a platable substrate; and a complexing agent. The complexing agent is advantageously an organic compound having between 4 and 18 carbon atoms which includes at least two hydroxyl groups and a five or six membered ring that contains at least one oxygen atom. The agent is present in an amount sufficient to complex the metal and render it soluble in the solution. In addition, the agent inhibits oxidation of the metal ion in the solution. When the metal ion has the ability to exist in the solution in at least two different valence states, the complex agent prevents oxidation of the metal from a lower valence state to a higher valence state. If necessary, a suitable pH adjusting agent can be included in the solution to maintain the pH of the solution in the range of above 3 but less than 6, and preferably between 3.5 and 5.5. The complexing agent and metal ion are present in a weight ratio sufficient to reduce or minimize agglomeration of the substrates during electroplating. A preferred ratio range is between about 3:1 and 9:1. At the most preferred pH range, the solution is particularly useful for electroplating substrates of composite articles that have electroplatable portions and non-electroplatable portions without deleteriously affecting the non-electroplatable portions.

The complexing agent preferably has one of the following the structures:



wherein each R is the same or different and is hydrogen or a lower alkyl group of 1 to 3 carbon atoms, T is R, OR, or $O{=}P(OR)_2$-, Z is O= or RO-, n is 2-4 and Z can be the same or different in each occurrence in the structure, and m is 1-3,

or the complexing agent is a soluble salt of such structure. The most preferred compounds include ascorbic acid, isoascorbic acid (also called erythorbic acid), dehydroascorbic acid, glucoascorbic acid, galacturonic acid, glucoronic acid, and glucose-6-phosphate, or a salt thereof. Typical salts include alkali or alkaline earth metals. These agents are generally present in an amount of about 25 to 200 g/l.

It has been found that the ratio of the complexing agent concentration to the tin and lead concentration is the primary factor which controls the agglomeration of the substrates or components during electroplating. Specifically, it is advantageous to provide only enough complexer to render the tin or lead soluble and to assure anode dissolution. A substantial excess of complexer has been found to cause agglomeration of components during plating. Therefore, one embodiment of the invention relates to the use of an amount of complexing agent in the solution in a specific ratio to the tin or lead ions such that only a small excess of free complexing agent is present in the plating solution. The exact ratio will depend on the complexer used as well as the solution pH.

The solution also may include a conductivity salt in an amount sufficient to increase the conductivity of the solution. Preferred conductivity salts are an alkali or alkaline metal sulfate, sulfonate, or acetate compound. A surfactant may be included in an amount sufficient to enhance deposit quality and grain structure. Also, an agent to promote anode dissolution can be used. This agent may be potassium methane sulfonate, ammonium chloride or a metal sulfide salt.

The invention also relates to a method for electroplating a metal deposit on composite articles that includes electroplatable and non-electroplatable portions. This method comprises contacting a plurality of such articles with one of the solutions described herein and passing a current though the solution to provide metal electrodeposits on the electroplatable portions of the articles

without deleteriously affecting the non-electroplatable portions of the articles. Preferred metal electrodeposits are tin metal or tin-lead alloys and the preferred articles are electronic components.

Brief Description of the Drawing

Further advantages of the invention are illustrated in the drawing figure, which is a graph of the results of a washer test, where the washer count is plotted against the ascorbic acid/tin concentration ratio.

Detailed Description of the Preferred Embodiments

It has now been discovered that the fusing of the composite article electronic components can be largely eliminated by providing an electrolyte which includes one or more of the complexing agents disclosed herein at a specific ratio to the tin or lead contained in the electrolyte. In particular, ascorbic acid and related compounds are the most preferred for use as such complexing agents.

The complexing agents are preferably utilized in solutions for electroplating tin or tin-lead deposits although they can also be used in solutions for electroplating other metals, particularly those metals that have multiple valence states. These complexing agents help maintain the metals in the solution at one of their lower valence states, thus facilitating the electroplating step and avoiding oxidation of the metals which can affect proper operation of the solution. Stannic tin is also complexed in these systems.

Any of the complexing agents of the formulae given above can be used in this invention. Advantageous complexing agents are organic acids, with preferred agents including ascorbic acid, isoascorbic acid, dehydroascorbic acid, glucoascorbic acid, galacturonic acid, and glucoronic acid. Salts of these acids can also be used, with the preferred salts being the alkali or alkaline metal salts. Ketogluconates can be used because these compounds convert in the bath to

ascorbic acid. Heptagluconates are also suitable since they convert in the solution to similar acidic species. Any of these agents can be used at a typical amount of about 25 to 200 g/l. The most preferred complexing agent is ascorbic acid or an ascorbate salt because these compounds have a relatively low cost and are readily available.

Ascorbic acid is included in the solution as simple ascorbic acid, an ascorbate salt such as sodium or potassium ascorbate, and/or as an ascorbic acid-metal complex, such as tin ascorbate for instance. The latter is preferred when it is desired to utilize other acidic components, such as organic acids or organic acid salts, to maintain the desired solution pH. The amount of ascorbic acid present should at a minimum be sufficient to render the metals present in the solution soluble at the given pH of the solution but should not greatly exceed this amount. As such the amount of ascorbic acid required is proportional to the metal concentration. At a tin concentration of 15 g/l, the preferred ascorbic acid concentration is about 80 to 120 g/l.

Tin metal is generally added to the solution as a stannous alkyl sulfonate salt, a stannous sulfate salt, a stannous chloride salt, a stannous ascorbate salt, or stannous oxide and is present in an amount of between about 5 and 100 g/l. When lead metal is added for the purpose of depositing a tin-lead alloy, it may be added to the solution as a divalent lead alkyl sulfonate salt, sulfate salt, chloride salt, or ascorbate salt and is present in an amount of between about 0.5 and 10 g/l.

The complexing agent is present in the solution in a specific concentration ratio to the tin or lead ions such that only the amount of complexing agent is just sufficient to complex the metals without providing significant excess amounts. While a small excess of free complexing agent may be present in the plating solution, large excesses must be avoided in order to prevent agglomeration of the substrates during electroplating. The exact ratio will depend on the complexer used as well as the solution pH. Typically, the

ratio is above 2:1 but is less than 10:1. Useful ratios range from about 3:1 to no more than 9:1. Also, higher pH values will require complexor to total metal concentration ratios of about 5:1 to 8:1 to maintain the metals in solution. The ratio in any specific case may be established by routine experimentation.

Any electroplatable substrates can be plated using the solutions of the present invention. Generally, these substrates are made of a metal such as copper, nickel, steel or stainless steel. In today's commercial products, many parts that require electroplating are being made in smaller and smaller sizes. In particular, electronic components are a typical example of such parts. Furthermore, these parts are composite articles that have electroplatable and non-electroplatable portions. While the metal portions are metals or metallic, the non-electroplatable parts are typically ceramic, glass or plastic. The present solutions are particularly useful for electroplating such composite articles.

The electroplating solutions should have a pH above 3 but less than 6, but preferably is in the range of about 3.5 and 5.5, and more preferably is about 4 to 5 so that the solution is compatible with the electronic components that are to be plated. When the components have metallic and inorganic portions, the preferred pH range enables metal to be deposited on the metallic portions without adversely affecting the inorganic portions. Generally, very high or very low pH solutions will damage the ceramic portions of the composite articles to be plated.

These solutions preferably do not contain appreciable amounts of free acid or free base, although essentially any acid or base can be used for pH adjustment. Generally, since the solution is acidic, a base or basic component is utilized to convert free acid to its corresponding salt. Preferred bases for this purpose include sodium or potassium hydroxide as well as many others.

The solution is formulated to be compatible with the substrates to be plated, and preferably to have no adverse effect on the substrates. When composite articles that have electroplatable and non-electroplatable portions are

to be plated, the solution should be formulated to not attack or crack the non-electroplatable portions of the substrates. A simple test can be used to determine substrate/solution compatibility. The articles to be plated can simply be immersed in the proposed solution for a period of time that is equal to or longer than that which is to be used for the plating process. The temperature of the solution can be that which approximates the temperature of the solution during the plating process, or an elevated temperature can be used for an accelerated test. The parts are immersed in the solution for a desired time and then are recovered and weighed to determine weight loss that occurs due to attack of the articles by the solution during immersion.

For example, composite articles used for capacitor manufacture now are being made with a low-fired ceramic. These ceramics contain a larger proportion of glass than conventional ceramics, and are more prone to attack during the plating process. A simple comparison test was made to determine the compatibility of various commercially available solutions and with a solution according to the present invention. The capacitors were placed into beakers containing equal amounts of these solutions, and weight loss of the parts after 5 hours immersion was measured. The results are shown in the following table:

Solution	Weight loss after 5 hours immersion in the solution (%)
Competitor A (gluconate based bath at pH of 3.5)	1.0%
Competitor A (gluconate based bath at pH of 4)	0.5%
Competitor B (citrate based bath with pH of 4.2)	5.0%
Present Invention (ascorbic acid bath with pH of 5)	0.0%

This table shows that the present invention has essentially no effect on the capacitors and is a substantial improvement for the plating of such components compared to conventional baths. It is theorized, that limiting the amount of

complexor to the amount required to complex the metal ions in the electroplating bath minimizes the attack of the metal oxide ceramic substrate by free complexor in the solution. This is a further advantage of the current invention.

A particularly useful device for electroplating such electrical components is disclosed in U.S. patent 6,193,858, and need not be described further herein. To the extent necessary, the entire content of that patent is expressly disclosed herein by reference thereto.

Improvements to the previously patented system have been disclosed in Published International Application WO02/053809, the entire content of which is expressly incorporated herein by reference thereto. The immersion of the plating chamber into the electrolyte, as disclosed in this application, represents a significant improvement in that external soluble electrodes can now be used.

It has been found that electrolytes which contain the complexing agents of the present invention are capable of electrodepositing tin or tin-lead alloys while minimizing the fusing or coupling of the electroplated parts, as well as without deleteriously affecting the non-electroplatable portions of the articles. In this regard, these electrolytes are superior to those of the prior art, and in particular to baths that are citrate based. The complexing agent serves to maintain the tin and/or lead in solution at the pH of the electrolyte. Certain complexing agents, in particular ascorbic acid, also serves as a stabilizer for preventing the oxidation of stannous tin to stannic tin.

L-ascorbic acid (AA) readily converts to L-dehydroascorbic acid (DAA). In addition, DAA can easily return to AA by the conversion of two ketone groups to hydroxyl groups on adjacent carbons with the single bond connecting those atoms being converted to a double bond. The ease in which AA converts to DAA renders AA a strong reducing agent. In the plating solutions of the present invention, AA assists in complexing the tin ions both in their divalent and tetravalent states. This prevents or at least minimizes the formation of tin

oxides that would precipitate to form sludge which deleteriously affects the performance of the solution.

A preferred solution according to the present invention comprises water, a divalent tin salt, and ascorbic acid as a complexing agent, and optionally contains a divalent lead salt, a salt to increase electrical conductivity, a surface active agent, or an agent to promote anode dissolution.

The stannous salts which may be used in this invention include stannous sulfate, stannous chloride, stannous oxide, stannous methane sulfonic acid, stannous ascorbate or any other suitable source of stannous tin. The stannous tin concentration in the solution maybe from 5 to 100 g/l and most preferably from 10 to 50 g/l. As noted above, the complexing agents of the invention also complex stannic salts, so that it is possible to add stannic salts to the solution instead of or along with stannous salts without concern.

The lead salts that may be optionally included to provide tin-lead deposits include any solution soluble divalent lead salt including, for example, lead methanesulfonate, lead acetate or lead ascorbate.

The conductivity of the solution maybe increased if necessary by the additional of a salt. If a pure tin solution is desired, a simple salt such as potassium sulfate may be used. If a tin-lead alloy is desired, potassium methanesulfonate or potassium acetate would be appropriate. Metal sulfide salts can also be used if desired. Any of these salts may be used to promote anode dissolution and assist in electrodeposition.

Surfactants which are typically utilized in tin or tin alloy electrolytes may be included in the solution to improve deposit crystalline structure and improve deposit quality at high current densities. Preferred surfactants include solution soluble alkylene oxide condensation compounds, solution soluble quaternary ammonium-fatty acid compounds, solution soluble amine oxide compounds, solution soluble tertiary amine compounds or mixtures thereof. One preferred surfactant is an alkylene oxide condensation compound and is present in an

amount of about 0.01 to 20 g/l. Other conventional surfactants can be used as there is no criticality to this component with regard to deposit appearance, although some additives may perform better than others with regard to coupling of the articles to be plated. One of ordinary skill in the art can perform routine testing to determine the most appropriate surfactants for any particular plating solution.

When bright deposits are desired, an aromatic aldehyde can be added in an amount sufficient to act as a brightener. Other conventional brighteners can instead be used if desired.

The substrates to be electroplated are preferably those composite articles that have conductive and non-conductive portions. While the metal portions are metals or metallic, the non-conductive parts are typically ceramic, glass or plastic. The present solutions are particularly useful for electroplating such composite articles without deleteriously affecting the non-metallic portions of the articles and without causing agglomeration or fusing of such parts.

The pH of the electrolyte is preferably retained in the range of about 4 to 5.5 when plating on composite substrate electronic components is desired. The pH can be raised by the addition of caustic, for example potassium hydroxide, ammonium hydroxide, sodium hydroxide or the like, or can be lowered with an acid such as sulfuric or methanesulfonic. An alkane or alkanol sulfonic acid, such as methanesulfonic acid, is preferred for tin-lead alloy solutions, since sulfuric acid can generate lead sulfate which is insoluble in the solution and which would tend to precipitate. As noted above, a pH of about 4 to 5.5 results in the strongest inhibition of agglomeration of such metals. Furthermore, the amount of ascorbic acid should not be in great excess to that needed to complex the tin in order to inhibit and minimize agglomeration.

Typical antioxidants used in tin and tin-lead solutions may be included in the solution of the present invention (e.g., catechol or hydroquinone as disclosed in US patent 4,871,429), however ascorbic acid has been found to be effective

in preventing the oxidation of stannous tin to stannic tin in neutral or near neutral pH plating solutions. As such, ascorbic acid serves the dual function of acting both as a complexing agent and as an antioxidant in the present solutions.

EXAMPLES

Example 1: A pure tin electrodeposit is obtained from the following solution and under the following electroplating conditions.

Tin (as a methanesulfonic acid salt)	15 g/l	
Ascorbic Acid	100 g/l	(Concentration ratio 6.67:1)
Surfactant	0.5 ml/l	

The pH was adjusted with KOH to 4.05.

The above solution will deposit semi-bright tin at current densities of up to 20 ASF.

Example 2: A semi-bright tin-lead deposit is obtained by adding 1.5g/l of lead methane sulfonate to the solution of claim 1 and plating at the same conditions.

Tin (as a methanesulfonic acid salt)	15 g/l	
Lead (as a methanesulfonic acid salt)	1.5 g/l	
Ascorbic Acid	100 g/l	(Concentration ratio 6.0)
Potassium methanesulfonic acid	40 g/l	
Surfactant	0.5 ml/l	

The pH was adjusted with KOH to 4.05.

This solution will also deposit semi-bright 90% tin at current densities of up to 20 ASF.

Example 3: The formulation of Example 1 was used to plate tin on 250 pieces of 8mm diameter flat washers in a 2.5" by 4"barrell, 140 ml of 2.5 mm diameter conductive balls were used as the media. The load was plated at 5A, 6.5V for 15 minutes. At the end of the plating cycle, none of the flat washers were fused together.

Example 4:

The same plating cycle as in Example 3 was conducted using an electrolyte of the following formulation:

Tin (as a methanesulfonic acid salt)	10 g/l	
Lead (as a methanesulfonic acid salt)	1.5 g/l	
Citric Acid	40 g/l	(Concentration ratio 3.5)
Potassium methanesulfonic acid	40 g/l	
Surfactant	2.5 ml/l	

The pH was adjusted with KOH to 4.2.

The load was plated at 5A and 9V for 15 minutes at the end of the plating cycle, and only 12 pieces were not coupled together. The remaining pieces were agglomerated in groups of up to 10 pieces and were difficult to separate. This example clearly demonstrates the superiority of the solutions of the present invention.

Example 5: Effect of concentration ratio on part agglomeration

The drawing figure illustrates the effect of the ascorbic acid to tin concentration ratio on part agglomeration during electroplating. Ascorbic acid baths having a pH of 4.2, 4.5 and 5 and using different ratios of ascorbic acid to tin were used to plate tin on 250 pieces of 8mm diameter flat washers in a 2.5" by 4"barrell, 140 ml of 2.5 mm diameter conductive balls were used as the media. The load was plated at 5A, 6.5V for 15 minutes. At the end of the plating cycle, the number of single washer and agglomerated washers were counted and summed. Therefore, a count of 250 represents that no washers were agglomerated. If all the washer were agglomerated into groups of two the count would be 125. As can be seen from the figure, lower ratios of ascorbic acid to tin result in less agglomeration. This effect is particularly pronounced at the lower pH values, as it is seen that higher complexer levels are required to maintain the tin in solution at higher pH values. Therefore, the higher pH value results are still consistent with the concept of limiting the amount of complexer in excess of that required to maintain the tin in solution.